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The Progress in Auger Electron Spectroscopy of Solids

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Abstract

The technique of Auger electron spectroscopy (AES) had its experimental beginnings in 1923 when Pierre Auger was studying the photoelectric effect in gases using a cloud chamber. He wanted to visualize the whole story of an atomic photoexcitation : (a) the production of a photoelectron, (b) the subsequent emission of a radiation quantum, and (c) the absorption of this quantum with the production of yet another photoelectron, all in the same cloud chamber. After the initial production of a photoelectron, he observed, however, that additional electrons emerged from the same point as the photoelectron, and he thought they might be due to the re-absorption of the radiation quantum by the same atom that produced it. By the time Auger published his thesis in 1926, he had realized that these extra electrons were not due to re-absorption but were due to a non-radiating transition, which had been predicted by Rosseland. These electrons emitted by non-radiative transitions have energies characteristic of the emitting atom and are now referred to as Auger electrons.

In the case of solids, humps in secondary electron distributions that were independent of primary electron beam energy were reported by Haworth in 1935. However, it was not until 1953 that certain peaks in secondary electron distributions were identified by Lander as due to Auger transitions. It was also pointed out by Lander that most elements could produce characteristic Auger electrons in the low energy range where the electron escape depth is small (several atomic layers) and that the excitation of Auger electrons would be an interesting technique for determining the composition of solid surfaces. Although the technique was used in some studies of surfaces, the difficulty in detecting the Auger peaks due to their superposition on a large, slowly varying background of secondary and backscattered electrons detracted from its usefulness at that time. In 1966, Tharp and Scheibner demonstrated that Auger peaks could be observed in the electron energy distribution from tungsten using a three-grid low energy electron diffraction (LEED) system and a lock-in amplifier.

In 1967, AES became a viable tool for surface analysis when Harris showed that electronic differentiation by synchronous detection methods using a lock-in amplifier enhanced spectral features which were not easily observed by more direct measurements in a deflection-type analyzer. Such spectra are referred to as derivative spectra . Shortly thereafter, Weber and Peria showed that these same derivatives could also be obtained using a three-grid LEED system. As such LEED systems were in widespread use at the time, the door was opened for research with AES, and this is when AES really took-off. LEED researchers were finally able to study the chemical compositions of surfaces, the details of surface cleaning methods, the adsorption of gases or deposition of metals on surfaces, and

to relate surface composition with surface structure. A good example was the application of AES to study the composition of the Si(111) 7X7 surface, to see if an impurity could be identified to cause this reconstruction of the surface.

The technique was further advanced in 1968 when Palmberg added a high current grazing incidence electron gun and an additional grid to the standard three-grid LEED system. The measurement of Auger spectra was also made easier with the introduction of a cylindrical mirror analyzer (CMA) in 1969. The improved signal-to-noise ratio of the CMA enhanced the sensitivity of the technique and made it possible to display Auger spectra covering a range up to 1000eV on an oscilloscope, allowing rapid acquisition of data.

In 1970, MacDonald published a paper where he added a coaxial cylinder spectrometer to a scanning electron microscope to demonstrate Auger electron chemical analysis with high spatial resolution. The following year he obtained two dimensional surface chemical analysis using a CMA in a computerized scanning electron microscope, and referred to this as an Auger electron image. Later, coaxial electron guns were mounted inside the inner cylinder of CMA s, and when equipped with deflection plates, provided the ability for Auger mapping. External electron guns were also provided with hemispherical electron energy analyzers for Auger analysis and mapping. Improvements in spatial resolution were made with electron gun design, including the addition of higher brightness electron sources. Today, Auger analysis can be accomplished on regions as small as a few 10 s of nanometers.

Argon ions had been used for sputter cleaning surfaces for LEED studies. It was only natural to add this to surface analysis systems to obtain the chemical composition with depth from a surface. In 1972, Tarng and Wehner published a paper showing the sputter depth profiles of molybdenum on different metals. The introduction of conically shaped fronts to CMA s allowed depth profiles to be obtained while sputtering in such systems. Depth resolution was always a problem in depth profiling, and many approaches were taken to improve the depth resolution. These include the ion beam energy, angle of incidence, multiple ion guns and specimen rotation. A special lecture on Experimental and Theoretical Depth Resolution Function in AES Depth Profiling is being given by Professor S. Hofmann.

When valence electrons are involved in the Auger process, changes in Auger line shape occur with change in chemical environment. This was recognized by Lander, but it was not until the late 1960 s that such effects were widely studied. Classic examples are the Auger line shapes exhibited by carbon in different chemical forms. Auger line shape variations can also occur for transitions involving core level electrons only, due to electron energy loss mechanisms. The kinetic energies of Auger transitions also change due to chemical effects.

With the introduction of small computers, Auger spectra are often acquired in the direct mode where the electron energy distribution is measured. Due to difficulties in routine background subtraction to isolate the Auger current, quantitative analysis is most often accomplished by differentiation of the direct spectrum and using peak-to-peak heights of the Auger features. Peak-to-peak measurements should be used only if the Auger line shapes are the same as a reference spectrum. Other factors in quantification include backscattering from the specimen and the instrument response function. Standard Auger spectra of copper, silver and gold have been measured. Quantification in AES is the subject of a special lecture by Dr. M.P. Seah.

Compilations of Auger spectra have been available since 1970, but one of the most exciting developments in AES is the rapidly increasing availability of electronic databases for Auger spectra, the biggest of which is that produced by the Surface Analysis Society of Japan which is available on the World Wide Web.

Auger spectra can also be produced by x-rays, ions and positrons, but these methods for excitation are not included in this presentation. Effects due to crystalline materials are also not discussed.

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